

GEL REDUCTION IN HIGH CIS-1,4 POLYBUTADIENE
PRODUCTION PROCESS

TECHNICAL FIELD

- 5 The present invention relates to an improved process for the production of polybutadiene having a high cis-1,4 content and a reduced gel content.

BACKGROUND ART

- 10 Processes for the production of polybutadiene having a high cis-1,4 content, generally known cis-1,4-polybutadiene, are well known. Such processes include the polymerization of 1,3-butadiene in an inert polymerization diluent using as catalyst a mixture of a transition metal salt, such as a cobalt salt, an aluminum alkyl halide or a mixture aluminum alkyl halides and water. During such processes, some gel is produced, such gel being essentially
15 insoluble particles containing cross-linked polybutadiene. The gel is not a desirable component due to the problems it can cause to equipment used for the production of the polymer and due to the problems it can cause relating to the quality of the cis-1,4-polybutadiene.

- 20 It is thus desirable to minimize and reduce to the lowest level possible the extent of gel formation during the polymerization process.

- 25 United States patent 3,094,514 teaches a process for the production of a cis-1,4-polybutadiene, having a cis-1,4-content greater than 90 per cent. Generally, the process comprises polymerization of 1,3-butadiene in a hydrocarbon diluent in the presence as catalyst of an anhydrous dihalide
30 diluent cobalt salt, a monoalkyl aluminum, and dialkyl aluminum monohalide. A similar type of process is described in United States patent 3,135,725. United States patent 3,646,001 teaches that cis-1,4-polybutadiene may be produced by polymerizing 1,3-butadiene in the presence of cobalt octoate and diethyl aluminum chloride which have been
30 reacted with benzene containing water. United States patent 4,224,426 teaches the polymerization of 1,3-butadiene to produce cis-1,4-polybutadiene

in the presence of a cobalt compound, at least one organo-aluminum chloride and water, the polymerization diluent being a mixture of C₅-C₈ cycloalkane, a saturated aliphatic hydrocarbon or an α -monoolefin, and an alkyl substituted benzene having 1 to 4 alkyl substituents. United States patent 5,397,851 teaches a process for the production of a cis-1,4-polybutadiene by the polymerization of 1,3-butadiene in an inert hydrocarbon diluent in the presence as catalyst of a diluent cobalt salt, an alkyl aluminum chloride, a tri-alkyl aluminum compound and water.

10 DISCLOSURE OF THE INVENTION

An objective of this invention is a process for the production of a high cis-1,4-polybutadiene having a very low level of gel content.

Accordingly, in one of its aspects, the present invention provides a process for the production of cis-1,4-polybutadiene having a low level of gel content, the process comprising the step of polymerizing 1,3 butadiene in the presence of a catalyst and a polymerization diluent, the polymerization diluent comprising an organic solvent and water particles having a median particle size less than or equal to about 10 μ m.

In one of its preferred embodiments, the present invention provides a process for the preparation of an essentially linear cis-1,4-polybutadiene having a very low level of gel content, the process comprising polymerizing 1,3-butadiene in the presence of a cobalt salt-organo aluminum halide-water catalyst system, the improvement being that the polymerization is carried out in the presence as polymerization diluent of a mixture of a C₅-C₆ cycloalkane and butene-1, a cobalt salt of an organic acid having 6 to 12 carbon atoms in the organic acid, an organo aluminum halide selected from (I) a mixture of (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesqui chloride and (b) an organo aluminum or formula R₃ Al wherein R is an alkyl group having 8 to 12 carbon atoms and (II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms, a polymerization modifier selected from 1,2-butadiene and 1,3-cyclo

octadiene, and water, said water having been mixed with at least a portion of said polymerization diluent such that the water is present in said polymerization diluent as particles having a median particle size less than or equal to about 10 μm .

- 5 Thus, the present inventor has discovered that controlling the median particle size of the water used in the diluent surprisingly and unexpectedly results in the production of high cis-1,4-polybutadiene having a relatively low level of gel content. Thus, the median diameter of the water particles used in the polymerization diluent is less than or equal to about 10 μm .
- 10 Preferably, the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm , more preferably from about 0.5 μm to about 6 μm , most preferably from about 1 μm to about 5 μm . The median particle size of the water particles may be determined in a conventional manner, for example, using a
- 15 Mastersizer™ particle size measuring system commercially available from Malvern Instruments Inc.

BEST MODE FOR CARRYING OUT THE INVENTION

- 20 Thus, the present process relates to the use of a polymerization diluent comprising an organic solvent and water particles.

 Preferably, the organic solvent is selected from the group comprising an aliphatic compound, an aromatic compound and mixtures thereof. The aliphatic compound may be selected from a saturated hydrocarbon, an unsaturated hydrocarbon and mixtures thereof.

- 25 Preferred saturated hydrocarbons may be selected from the group comprising $\text{C}_4\text{-C}_{10}$ aliphatic hydrocarbon, a $\text{C}_5\text{-C}_{10}$ cyclic aliphatic hydrocarbon, a $\text{C}_6\text{-C}_9$ aromatic hydrocarbon, a $\text{C}_2\text{-C}_{10}$ monoolefinic hydrocarbon and mixtures thereof.

Non-limiting examples of a suitable C₂-C₁₀ monoolefinic hydrocarbon
5 may selected from the group comprising butene-1, pentene-1, hexene-1 and
mixtures thereof.

Non-limiting examples of a suitable C₅-C₁₀ cyclic aliphatic hydrocarbon may be selected from the group comprising unsubstituted cycloalkanes, methyl substituted cycloalkanes, ethyl substituted cycloalkanes and mixtures thereof.

Non-limiting examples of a suitable C₅-C₁₀ cyclic aliphatic hydrocarbon is selected from the group comprising cyclopentane, cyclohexane, cyclooctane and mixtures thereof.

15 Non-limiting examples of a suitable a C₆-C₉ aromatic hydrocarbon may be selected from the group comprising benzene, toluene, xylene and mixtures thereof.

The most preferred organic solvent for use in the present process comprises a mixtures of cyclohexane and butene-1.

20 Preferably, the polymerization diluent further comprises a
polymerization modifier. The use of such a modifier allows for controlling
the molecular weight of the polymer product. Illustrative examples of useful
polymerization modifiers for use in the present process may be selected from
the group comprising C₂-C₁₈ non-conjugated dienes, C₆-C₁₂ cyclic dienes and
mixtures thereof. Non-limiting examples of suitable polymerization
25 modifiers may be selected from the group comprising 1,2-butadiene, 1,3-
cyclooctadiene, 1,5-cyclooctadiene and mixtures thereof. The amount of
polymerization modifier may be from about 1.6 to about 3.5, preferably
from about 1.95 to about 3.0, millimols per mole of 1,3-butadiene in the
polymerization mixture.

The choice catalyst that is employed in butadiene polymerization art are well known. Preferably, the catalyst comprises a substantially anhydrous cobalt salt and an organo-aluminum halide compound.

5 The substantially anhydrous cobalt salt may comprise a compound having the formula CoA_m , wherein A is selected from a monovalent anion and a divalent anion, and m is 1 or 2. Preferably, the anion is derived from a $\text{C}_6\text{-C}_{12}$ organic acid. Thus, non-limiting examples of usefully such anions may be selected from the group comprising an acetylacetonate, an acetate, a hexanoate, an octoate, an oxalate, a tartrate, a stearate, a sorbate, an adipate
10 and a naphthenate.

The most preferred substantially anhydrous cobalt salt for use in the present process is cobalt octoate.

Preferably, the organo-aluminum halide compound comprises a compound having the formula:

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wherein: R is a $\text{C}_2\text{-C}_{12}$ alkyl group, X is a halogen and $p+q$ is 3.

20 More preferably, the organo-aluminum halide compound is selected from the group comprising a dialkyl aluminum chloride compound, an alkyl aluminum sesquichloride compound and mixtures thereof.

Even more preferably, the organo-aluminum halide compound is selected from:

25 (I) a mixture of: (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride (this may be achieved by a mixture containing approximately equimolar amounts of diethyl aluminum chloride and ethyl aluminum dichloride), and (b) an organo aluminum compound of formula R_3Al wherein R is $\text{C}_8\text{-C}_{12}$ alkyl group (e.g., trioctyl aluminum, tridecyl aluminum and the like); and

(II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms (e.g., dioctyl aluminum chloride, didecyl aluminum chloride and the like).

Embodiment (I) is more preferred. In this preferred embodiment, it is especially preferred to use the organo aluminum compound of formula R_3Al is present in an amount of 0 to 1 percent by weight of the mixture of (I) and (II). The preferred organo aluminum compound of formula R_3Al comprises tri-octyl aluminum.

The preferred catalyst system for use in the present process comprises a cobalt salt selected from cobalt octoate and cobalt naphthenate, and an organo aluminum halide compound selected from: (i) a mixture of diethyl aluminum chloride and one or more of trioctyl aluminum, tridecyl aluminum and tridodecyl aluminum, and (ii) one or more of dioctyl aluminum chloride, didecyl aluminum chloride and didodecyl aluminum chloride.

In a preferred process, using cyclohexane and butene-1 as the diluent the weight ratio of butene-1 in the cyclohexane-butene-1 mixture may be from about 24 to about 40, preferably from about 24 to about 38 and most preferably from about 34 to about 36, weight percent. A preferred catalyst cobalt octoate which is used with a preferred organo aluminum halide compound which is a mixture of diethyl aluminum chloride and trioctyl aluminum, wherein the molar ratio of cobalt octoate to the total of the diethyl aluminum chloride plus trioctyl aluminum is from about 1:15 to about 1:30, preferably from about 1:15 to about 1:20 and wherein the molar ratio of chlorine in the diethyl aluminum chloride to the total aluminum in the diethyl aluminum chloride plus trioctyl aluminum is from about 0.7:1 to about 0.95:1, preferably from about 0.8:1 to about 0.9:1.

The amount of 1,3-butadiene in the 1,3-butadiene plus diluent mixture may be from about 15 to about 35, preferably from about 25 to about 35, weight percent.

The polymerization mixture also contains water. The amount of water is from about 0.3 to about 0.8, preferably from about 0.5 to about 0.65, millimols per millimol of the alkyl aluminum chloride used. The water is mixed with at least a portion of the polymerization diluent. Accordingly, in the preferred diluent comprising cycloalkane and butene-1, the water may be mixed with cycloalkane alone, or, preferably with cycloalkane and butene-1 mixture. The mixing of the water with the polymerization diluent is such that the water as present in the polymerization diluent as particles having a median particle size equal to or less than 10 μm . Because of the very low solubility of water in hydrocarbons, including the polymerization diluents, and because of the long time to achieve a solution of water in such hydrocarbons, it is desirable for the present polymerization system to disperse the water in the polymerization diluent as very small particles to provide as high as possible a surface area to weight ratio for the particles so that interaction with the aluminum compound(s) is as efficiently as possible - this is believed to be important in reducing the amount of gel in the polybutadiene produced. The dispersion of water in the polymerization diluent may be achieved by various means such as, but not limited to, mechanical methods and sonic treatment. The improvement of the present invention is not dependent on the method used to obtain the dispersion of water in the polymerization diluent and is only dependent on the median diameter of the water particles used in the polymerization diluent being less than or equal to about 10 μm . Preferably, the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm , more preferably from about 0.5 μm to about 6 μm , most preferably from about 1 μm to about 5 μm .

The polymerization may be undertaken at a temperature of from about -10°C to about 50°C , preferably from about 5°C to about 40°C and most preferably from about 15°C to about 35°C . The polymerization process may be carried out in a batch process or in a continuous process, the continuous process being preferred. The reaction time for the

polymerization may be from about 20 to about 90 minutes, preferably from about 25 to about 60 minutes. However, the reaction time is not a critical aspect of the process and may be affected by the desired conversion of the 1,3-butadiene to polymer which may range from about 40 to about 90 percent.

The gel content of the polymer may be determined by a method in which the gel is separated from a solution of the polymer in styrene and weighed. In detail, approximately 50 g of polymer, accurately weighed, is dissolved in pure, filtered styrene to produce an approximately 4 weight percent by volume solution. The polymer-styrene mixture is shaken for 4 to 5 hours, then allowed to stand for 10 minutes and then filtered through a previously weighed filtration screen of 400 mesh. The filtration screen is then weighed again and the amount of wet gel is calculated as parts per million by weight based on the original weight of polymer used. Gel contents of less than about 250 ppm are desirable and less than about 150 ppm are more desirable and less than about 100 ppm are most desirable. In order to provide the greatest accuracy to the gel content of the polymer, normally at least three and up to 5 samples of the polymer are used to provide the corresponding number of gel content measurements.

In the following examples, the 1,3-butadiene was obtained from Union Carbide, the cyclohexane and butene-1 was Phillips pure grade and all three were passed through a column containing 4A molecular sieves followed by passage through a column containing 13X molecular sieves before use in polymerization. The 1,3-cyclooctadiene was used as a 20 weight percent solution in cyclohexane from Aldrich Chemical Company. Diethyl aluminum chloride in hexane as a 1 molar solution was from Albemarle Corporation and Akzo Nobel. Tri-octyl aluminum in heptane (20% wt.) was obtained from Albemarle Corporation as a 25.3 wt.% solution. Cobalt octoate was obtained from Mooney Chemical Inc. and used as a 6% cobalt solution in cyclohexane. Diethyl aluminum chloride was mixed with tri-octyl aluminum in sealed bottles under an inert gas in such ratios as to

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provide a solution having an average composition of $\text{Et}_{1.8}\text{Oct}_{0.3}\text{Al}_1\text{Cl}_{0.9}$ in cyclohexane which was used in all examples and is referred to as M-DEAC. Polymerization was undertaken in sealed 1 litre polymerization bottles at a temperature of 27°C for 40 minutes at the end of which time the

5 polymerization was stopped by the injection of 5 ml of ethanol containing required amount of stabilizer and the polymer was recovered by steam coagulation.

Embodiments of the present invention will be illustrated with reference to the following Examples which should not be used to limit or

10 construe the scope of the invention.

EXAMPLE 1

Using 1 liter glass bottles capped with gasketted crown caps, 110 g of cyclohexane, 80 g of 1,3-butadiene, 60 g of butene-1, 1.8 mL of a 20%

15 solution of 1,3-octadiene in cyclohexane, 0.01 mL of pure distilled water, 0.54 mL of a 25% solution of M-DEAC and 0.19 mL of a 0.25% solution of cobalt octoate in cyclohexane were charged to the glass bottles. When the cobalt octoate was added, the glass bottles were placed in an agitated polymerization bath maintained at 27°C for 40 minutes, followed by addition

20 of ethanol to stop polymerization. The polymer was recovered and dried and samples used to measure the gel content, with the results shown in Table 1.

With reference to Table 1, Experiment #1 is a control in which the cyclohexane plus water was shaken for 5 minutes which produced clearly visible particles (median much greater than 10 μm) of water in the

25 cyclohexane. The other components were added after the shaking.

In Experiment #2, the cyclohexane and water was subjected to sonification for 5 minutes in a Branson™ ultrasonic cleaner which produced a mixture of water particles in cyclohexane in which the water particles had a median particle size of less than 10 μm . The other components were added

30 after completion of the ultrasonic mixing.

In Experiment #3, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to sonification as described above; the water particles had a median particle size of less than 10 μm . The other components were added on completion of the ultrasonic mixing.

- 5 In Experiment #4, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to shaking for 48 hours producing water particles having a median particle size of less than 10 μm . The other components were added on completion of the shaking. The gel data provided in Table 1 clearly show that the presence of water particles having a median particle
- 10 size of less than 10 μm resulted in the production of polymers having significantly reduced gel contents.

TABLE 1

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Experiment #	1	2	3	4
Gel (ppm)	1200	15	80	95
	1540	28	56	82
	1010	32	110	100
	1610	26	75	73
	-	30	100	-
Average Gel (ppm)	1340	26	84	87

20 EXAMPLE 2

- Using the procedure and components described in Example 1, polymerizations were undertaken in which the cyclohexane, 1,3-butadiene, butene-1, water and M-DEAC were mixed by shaking for a period ranging from 0 to 30 minutes. The other components were added on completion of
- 25 the shaking. The gel results shown in Table 2 show that when the median

particle size is reduced less than 10 μm , the gel content of the polymer is significantly reduced.

TABLE 2

Shaking Time (min)	Water Particle Size (μm)	Gel (ppm)
0	-	2950
5	-	1680
10	-	863
15	-	520
20	-	120
25	< 10	50
30	< 10	38

EXAMPLE 3

Using the procedure described in Example 1, the following experiments were undertaken. 110 g of cyclohexane and 0.011 mL of water was subjected to sonification for 5 minutes producing a mixture containing particles of water having a median particle size of less than 10 μm .

Following this, 80 g of 1,3-butadiene, 2.0 mL of a 20% solution of 1:3 cyclooctadiene in cyclohexane, 60 g of butene-1, 1.25 mL of a 12% solution of diethyl aluminum chloride in cyclohexane and 0.2 mL of a 0.25% solution of cobalt octoate in cyclohexane were added and the contents immersed in an agitated water bath at 27°C for 40 minutes. After stopping the polymerization, the polymer was recovered and the gel content was determined to be 120 ppm. In a control experiment, the same procedure was followed except that instead of being sonified, the cyclohexane and water

was mixed by shaking. The water particles were found to have a median particle size of greater than 10 μm . The resulting polymer was found to have a gel content of greater than 3000 ppm.

- 5 All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

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